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Effect of Diluted Colloidal Silica Slurry Mixed with Ceria Abrasives on CMP Characteristic

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KEYWORDS: Colloidal silica slurry, Mixed abrasive slurry(MAS), Ceria, Dilution slurry, Chemical mechanical polishing(CMP)

In this paper, we have studied the CMP characteristics of mixed abrasive slurry (MAS) retreated by adding of ceria abrasives within 1:10 diluted silica slurry (DSS). We focused on how these mixed ceria abrasives affect the material removal in order to determine the optimal recipe conditions through the correlation between the mixed contents of ceria abrasives and CMP performances. The slurry designed for optimal performance should produce reasonable removal rates, acceptable polishing selectivity with respect to the underlying layer, low surface defects after polishing, and good slurry stability. The modified abrasives in MAS are evaluated with respect to their particle size distribution, surface morphology, and CMP performances such as removal rate and non-uniformity. As a result, the oxide CMP process using diluted mixed abrasive slurry has problems of higher material removal rate at wafer center. But, we solved the questions in consecutive order by pH control. We obtained the comparable slurry characteristics to original silica slurry in the viewpoint of high removal rate and low non-uniformity. Finally, our proposed ceria-MAS can be useful to save a slurry consumption of high cost since we used 1:10 diluted mixed abrasive slurry.

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1. Introduction

Chemical mechanical polishing (CMP) has become one of the most important technologies for producing nano-scale semiconductor devices because it meets the stringent requirements for ever increasing integrated intensities and yields. CMP process has been widely used to obtain the global planarization of inter-metal dielectric (IMD) layers, inter-layer dielectric layers (ILD) and pre-metal dielectric (PMD) layers.[1-5] In general, chemical compositions and abrasives of the slurry play a very important role in the removal rate and within-wafer non-uniformity for global planarization ability of CMP process. The conventional slurry consists of abrasive particles of the solid state suspended in a liquid state-chemical solution. The abrasive in the slurry transfers mechanical energy to the surface being polished and plays a key role in its material removal. In the manufacturing process for ULSI chip, the abrasive of widely used slurry is silica (SiO_2) and alumina ($Al2O_3$). Ceria (CeO_2) has been more commonly used for glass polishing, and recently for oxide films for shallow trench isolation (STI) structure. Through chemical reaction and mechanical action, the abrasive-liquid interaction plays an important role in determining the optimum abrasives type and size, their shape and concentration.[6,7] The slurry was designed for optimal performance which produced reasonable removal rates, acceptable polishing selectivity with respect to underlying layer, low surface defects after polishing, and good slurry stability.[8] One of the most critical problems is the higher cost of consumables (COC) such as pad, slurry, backing film, and pad conditioner which accounts for over 70% of cost of ownership (COO). Since a sufficient amount of slurry is required to get a higher removal rate (RR) and lower within-wafer non-uniformity (WIWNU), there have recently been many studies on the reduction of slurry consumption since the cost of the slurry is about 40% of COC. Total slurry revenues will grow at a compound annual growth rate (CAGR) of 8.2% between years 2008 and 2014. This must be factored into the changing landscape between low-cost ILD slurry, which is in decline compared to high-priced metal and ceria-based shallow trench isolation (STI) slurry. Revenues generated will grow from $874 million in the year 2008 to $1,402 million in 2014. The volume of slurry will grow at a CAGR of 16.8% from 1.4 million 55 gallon drums in 2008 to 3.6 million in 2014.[9]

In this paper, we have studied the CMP characteristics of mixed abrasive slurry (MAS) retreated by adding of Ceria (CeO_2) abrasives within 1:10 diluted silica slurry (DSS). We focused on how these mixed ceria abrasives affect the material removal in order to determine the optimal recipe conditions through the correlation between the mixed contents of ceria abrasives and CMP performances in our self-developed. In this work, slurries containing CeO_2 abrasives and SiO_2 particles dispersed in DIW at pH 5-11 were studied for the oxide CMP process. The modified abrasives in the MAS were evaluated with respect to their CMP performances such as removal rate and non-uniformity and peak to valley roughness. Our main goal is to examine how these mixed two particles affect the CMP characteristics of oxide layer.

2. Theory

2.1 Single Abrasive Slurry (SAS)

When the SiO_2 particles are dispersed in an aqueous alkaline solution, the OH^- ions are selectively adsorbed on the SiO_2 particle surface, and the Si-O bonds are dissociated as shown in Eq. 1.[1,10-12]

$$\equiv\text{Si-O-Si}\equiv + OH^- \rightarrow \equiv\text{Si-OH} + {}^-\text{O-Si} \quad (1)$$

Eventually, the SiO_2 particle surface is negatively charged. The positive ions, which are diffused in the slurry liquid, surround the SiO_2 particles to neutralize the negative surface charges. Verwey and Overbeek calculated the potential energy (V) between the particles as the sum of the repulsive (V_R) and the attractive potentials (V_A) as shown in Eq. 2.[11,13]

$$V = V_R + V_A \quad (2)$$

If the repulsive potential energy decreases down to the attractive potential energy, such as $|V_R|<|V_A|$, the particles tend to agglomerate. When the large particles, which originate from the agglomeration of slurry, come in contact with the wafer surface during polishing, micro-scratches cause a circuit failure and affect the yield of devices.[14,15]

2.2 Mixed Abrasive Slurry (MAS)

The polishing mechanism by both abrasives in MAS, consists of two types of abrasive particles, has been reported by S. V. Babu and his laboratory members.[16,17] When two types of particles are dispersed together, additional particle-particle interactions occur. And they can influence the interaction between the particle and film during CMP, which can be adjusted to optimize the slurry performance in terms of removal rate and surface defect.[18-22] One of examples is to disperse mechanically larger CeO_2 particles in the slurry containing relatively smaller SiO_2 particles. This dispersion has enough abrasion capability for material removal without surface defect. That is to say, there is improved CMP performance of MAS due to the interplay between the abrasive action of the CeO_2 particles and chemical-tooth nature of the SiO_2 particles surrounding the CeO_2 particles. Fig. 1 show the schematic diagrams of agglomeration and dispersion effects of MAS.

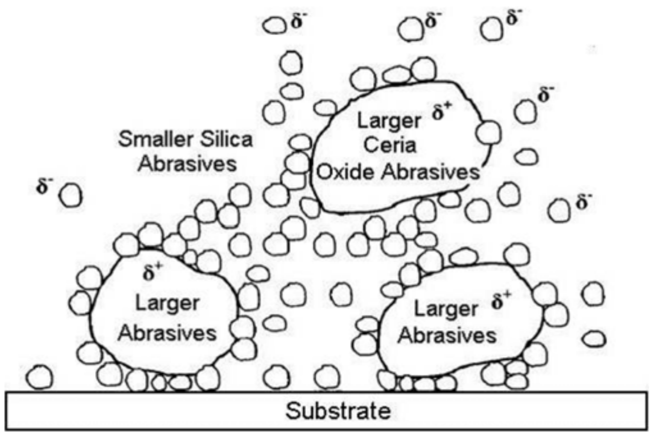

Fig. 1 Schematic of the proposed polishing mechanism by abrasive in mixed abrasive slurry

3. Experiments

The CMP setup and procedure have been described elsewhere.[1,14,18-26] In brief, in order to prepare the MAS, colloidal silica slurry of pH 11 was diluted in DIW with 1:10 ratio. Nitric acid and KOH was added as a buffering agent to keep pH 5 and pH 11 level controlled. The CeO_2 abrasives particles were then added in the diluted silica slurry. We have prepared the four kinds of slurry in order to compare the effect of agglomeration and dispersion on polishing efficiency. The concentration of CeO_2 abrasive was varied from 0.1 wt% to 9 wt%. The particle size distribution of the slurries was measured by using a Zeta potentiometer from Otsuka electronics Co. An oxide layer of 20,000Å was deposited on 4-inch blanket wafer. The CMP polishing of all test wafers was performed with a G&P POLI-500 CMP polisher. The polishing pad was an IC-1400 from Dow electronic materials. A diamond pad conditioner was utilized to abrade the pad before conducting each polishing test. The parameter range of the optimized CMP process was summarized in our previously published papers.[21,25] Table 1 shows the process conditions as functions of ceria abrasive addition. A ST-5030SL system of the K-MAC company was used to measure the oxide thickness. The surface roughness of the polished wafers was obtained using atomic force microscopy (AFM; PSIA, XE-100) technique.

4. Results and Discussion

Slurry using CeO_2 particles does not have dispersibility than the existing silica slurry, but has many merits such as high selection ratio, so commonly used in CMP process. However, ceria CMP has high

Table 1 Process condition as a function of CeO_2 abrasive addition

Table speed	80 rpm
Head speed	80 rpm
Pressure	300 g/cm^2
Slurry flow rate	120 mL/min
Polishing time	60 sec
Ceria powder, mean diameter 200-250 nm	0.1, 0.5, 1, 3, 5, 7, 9 wt%
KOH or HNO_3	To adjust pH 4, 5, 6, 8, 10
Stirrer	In-Situ
Wafer	4 inch thermal oxide thickness 20,000 Å
Silica particle size	100-150 nm

wafer center removal rate (RR) and shows different behaviors comparison to silica particles (e.g. causing a loading time). This is an outcome that is not seen when silica particles are used, which becomes the main cause that worsens uniformity after the CMP. As a result, ceria slurry has a polishing mechanism through the reaction of condensation between the silanol group and the ceria particle surface. It has a reaction formula in the form of Ce-OH + -Si -OH Ce-O-Si- + H_2O, and when CeO_2 particles are used, it has a CMP mechanism of oxide chemical tooth. This is because a strong chemical interaction affects between ceria and silica, and chemical aspects are more important as compared to silica particles.

Fig. 2 shows the comparison of removal rate and profile as a function of CeO_2 abrasive addition amount of pH 12-12.5. It is well known as the center fast aspect of material removal rate. Therefore, the slurry accumulation in the wafer center can be predicted during CMP. Also, another reason is that the specific gravity of dispersed CeO_2 abrasives is higher than that of silica abrasives. As shown in the result, the average polishing rate showed the amount of removal of 1360 Å/min when the slurry was diluted, but when 0.1 wt% CeO_2 particles were added after dilution, the amount of polishing tended to decrease. However, the more the amount of addition of CeO_2, the more the polishing rate became, according to the amount of addition, but the polishing rate in the center of the wafer showed higher polishing rate than the edge of it did. Fig. 3 shows uniformity according to the amount of addition of CeO_2, and the more the amount of addition, the less the uniformity tended to become. This seems that, as described above, a strong chemical interaction affects between CeO_2 and silica. The dispersed liquid of CeO_2 particles basically has neutrality.

Figs. 4 and 5 show the comparison of removal rate and non-uniformity as a function of pH control in the ceria abrasive addition of 9 wt%, respectively. Fig. 4 shows RR and non-uniformity (NU%) when oxide CMP was conducted, changing the pH by adding KOH and HNO_3. Oxide RR has pH 8, and in acid area, one with lower pH, RR tended to decrease. For silica particles, as pH increases to base, RR increases, but CeO_2 particles have the maximum RR in the weak base area. RR gets lower in acid because pH is in acid area, the degree of dissociation of the silanol group gets lower, so it is difficult to have a polishing mechanism of chemical reaction of condensation with the ceria particle surface.[6] Fig. 5 shows NU% data by pH. As it changes from alkali area to acid area, it shows much better result in terms of non-uniformity. Generally, the typical non-uniformity of the insulating film, metal film, and metal oxide film have to be below 5.0% in order to obtain stable characteristics of a CMP process.

Three-dimensional surface morphology of the polished oxide layer are shown in Fig. 6, where the layer was polished by CeO_2 adding

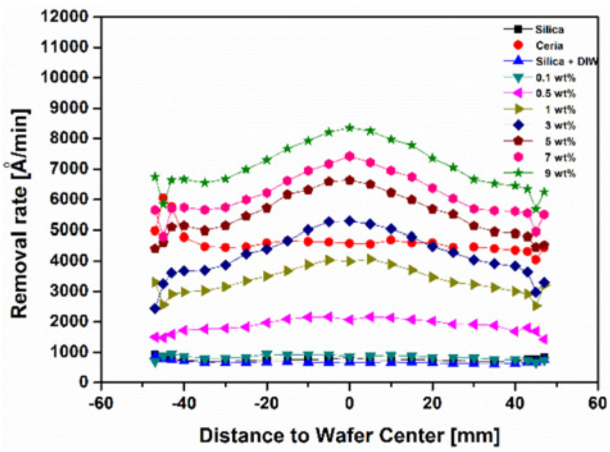

Fig. 2 Removal rate and profile as a function of CeO_2 abrasive Addition

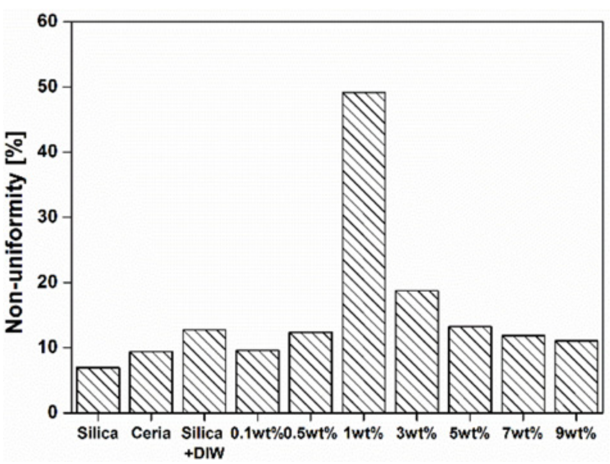

Fig. 3 Non-Uniformity as a function of CeO_2 abrasive addition

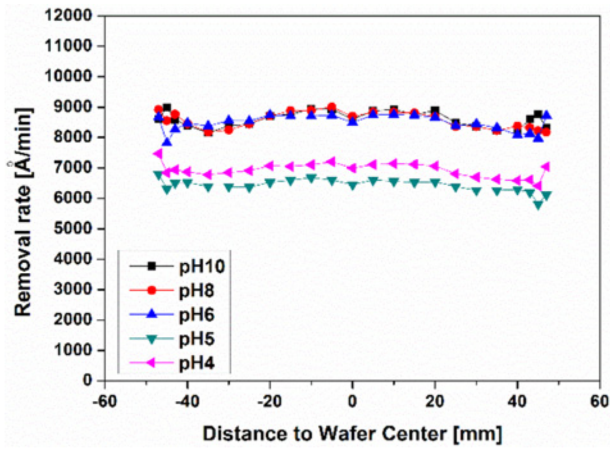

Fig. 4 Removal rate and profile as a function of pH controlled and CeO_2 abrasive addition

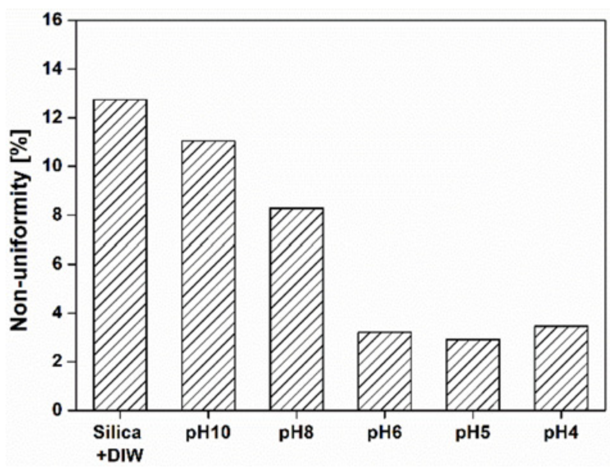

Fig. 5 Non-Uniformity as a function of pH controlled and CeO_2 abrasive addition

slurry (a) Ceria slurry, (b) Silica slurry, (c) Silica + DIW, (d) Ceria pH 10-MAS, (e) Ceria pH 8-MAS, (f) Ceria pH 6-MAS, (g) Ceria pH 5-MAS and (h) Ceria pH 4-MAS, respectively. These surface photographs showed that deep scratches are not formed at these surfaces when polished by CeO_2-MAS employed in a different content. Fig. 6(f) shows

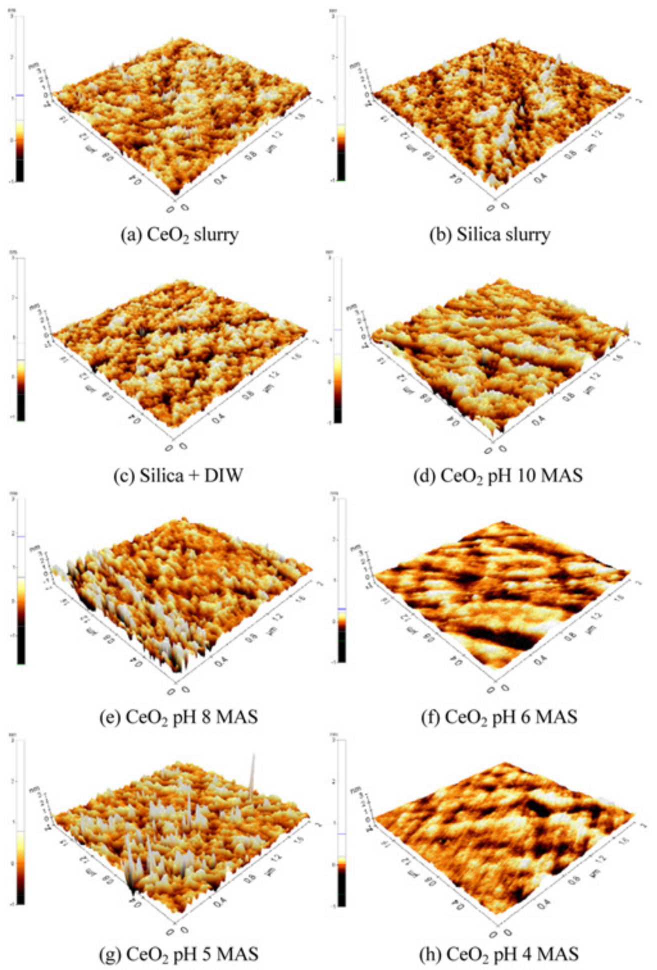

Fig. 6 AFM surface 3D images and scan profiles as a function of the pH controlled and CeO_2 abrasive contents. (a) CeO_2 slurry, (b) Silica slurry, (c) Silica + DIW, (d) CeO_2 pH 10 MAS, (e) CeO_2 pH 8 MAS, (f) CeO_2 pH 6 MAS, (g) CeO_2 pH 5 MAS, and (h) CeO_2 pH 4 MAS

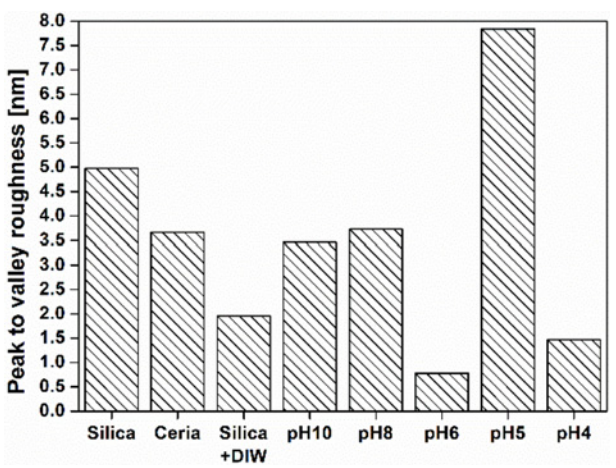

Fig. 7 Peak to valley roughness as a function of the pH controlled and CeO_2 abrasive contents

that the more smoothened surface can be prepared by polishing with pH 6 content. Because deep scratches were not induced by this polishing, this polishing is useful for the oxide CMP process. Also, the polishing profile as a function of pH control for the case of ceria addition amount of 9 wt% showed more stable state in comparison of other samples. The roughness of surface was determined quantitatively by the AFM measurement. The surface roughness was defined by peak to valley roughness (Rpv) value. Fig. 7 compares the Rpv values of surface polished by CeO_2-MAS with a different abrasive content. For the case of pH 5 CeO_2-adding, the high Rpv value of 7.8 nm was obtained.

5. Conclusions

This study was performed, aiming at a method for reducing the cost of consumables (COC) based on the background theory of CMP processing and producing equal cost of performance (COP) for undiluted solution slurry. As for the elements affecting CMP characteristics, in addition to an impact by consumables, there is an impact by CMP equipment, but this study looked into the impacts of the elements on CMP characteristics when the slurry was diluted, which accounted for over 40% of the consumable goods of the constituent. In terms of polishing rate and heterogeneity of oxide film, it was found that it shows more excellent characteristics than those of ceria undiluted solution slurry. Thus, it can save the slurry that bears the most cost during CMP process, so it is expected that it can reduce the cost of processing and manufacturing to improve productivity, and for the precision polishing process with minute pattern, first carrying out polishing process using the mixed polishing slurry proposed in this study and then polishing using undiluted solution slurry may make the process of processing somewhat complicated, but relatively expensive slurry consumption may be reduced. Finally, it is expected that applying this to CMP processing of metals such as Cu, Al and W or printed circuit board (PCB) CMP processing using noble metal or massive slurry, in which it takes much time to process polishing will bring about an effect on saving the processing cost to a half or more and improve productivity.

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